

Scandium(III) Coordination Polymers Containing Capsules Based on Two *p*-Sulfonatocalix[4]arenes

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Abstract: Reactions of sodium *p*-sulfonatocalix[4]arene and scandium(III) *tris*-triflate in the presence, and absence, of [18]crown-6 give the crystalline complexes $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_{10}][\text{Na}_4(\text{H}_2\text{O})_8\text{-calix[4]arene}(\text{SO}_3)_4]_2 \cdot 13\text{H}_2\text{O}$ and $\{[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_8][\text{Sc}(\text{H}_2\text{O})_4]_2[\text{calix[4]arene}(\text{SO}_3)_4\text{-H}^+]_2[\text{18crown-6}]\} \cdot 16\text{H}_2\text{O}$. Both complexes involve novel coordination polymers with calixarene units linked through sodium or scandium centers and also feature capsule assemblies through to the head-to-head asso-

ciation of calixarenes. A linear array of capsules associated with an infinite chain of aquo-bridged sodium ions, and an aquated hydroxy-bridged scandium(III) dimer, $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_{10}]^{4+}$, are found in the absence of the crown ether. In the presence of [18]crown-6 both hydrated scandium monomers and dim-

ers bridge between calixarenes in a two-dimensional coordination network. The crown ethers reside in cavities created by two calixarenes from adjacent polymeric sheets *via* a variety of supramolecular interactions (hydrogen-bonding, shape complementarity), and effectively add a third dimension to the network. The extended structure of both of these polymers is highly porous, and resembles a bilayer.

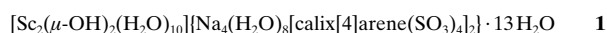
Keywords: calixarenes • coordination polymers • host–guest systems • scandium

Introduction

Calixarenes are potentially versatile synthons for the formation of coordination polymers. They can be designed with sites available for metal binding on the upper and lower rim, as well as at the linker positions, and are available in a range of ring sizes and conformations that could be used to influence the topology and function of networks formed.^[1] As the bowl-shaped calixarenes have well-documented inclusion properties, coordination polymers formed from them may lead to the development of useful chemoselective materials. Despite this, there are only a few examples in which calixarenes of any sort participate in coordination polymers. These include Ag^+ ions linking substituted calix[4]arenes in the 1,3-alternate conformation in a one dimensional array,^[2] and Cu^{2+} coordination linking a cone-shaped calix[4]arene in a linear array.^[3] Similarly, metal ions such as those of Ti, Nb, Al, Zn, Mo, and Eu can bridge two cone-shaped calixarenes to form ditopic receptor molecules or koilands. These are suitable for binding a range of guests which are then used to build up linear host–guest networks.^[4]

Despite their interesting electronic and magnetic properties and high coordination numbers^[5] there are relatively few examples of rare-earth cations used in coordination polymers. For the smallest rare-earth ion, scandium, there are a few examples based on relatively simple oxygen donor ligands.^[6] Previous studies have shown that *p*-sulfonatocalixarenes are able to compete with water molecules to ligate to the hydrophilic rare-earth ions. As a result a number of discrete supramolecular assemblies that incorporate the rare earth cations and *p*-sulfonatocalix[4] and -[5]arenes have been isolated,^[7–10] some of which feature head-to-head dimerization of the calixarenes to form a capsule assembly. The formation of such capsules usually occurs with the calixarenes shrouding a guest molecule, such as the [18]crown-6,^[8] with numerous supramolecular interactions such as hydrogen bonding and a complementarity of curvature between components of the capsule. The extended structure of rare-earth metal:calixarene assemblies often conforms to a claylike bilayer in which the calixarenes pack in an up/down fashion to form alternating hydrophilic/hydrophobic seams.^[9] Notable exceptions include the complexes formed in the presence of pyridine *N*-oxide, and the Al^{3+} keggion.^[10, 11]

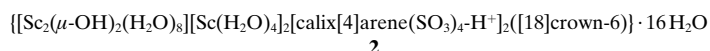
The interaction between scandium and *p*-sulfonatocalixarenes has remained unexplored. In the present study, the assembly of Sc^{3+} and *p*-sulfonatocalix[4]arene as its sodium salt was explored in the presence, and absence, of [18]crown-6. When the rare-earth reacts with the calixarene, a one-dimensional coordination array results within the complex **1**.



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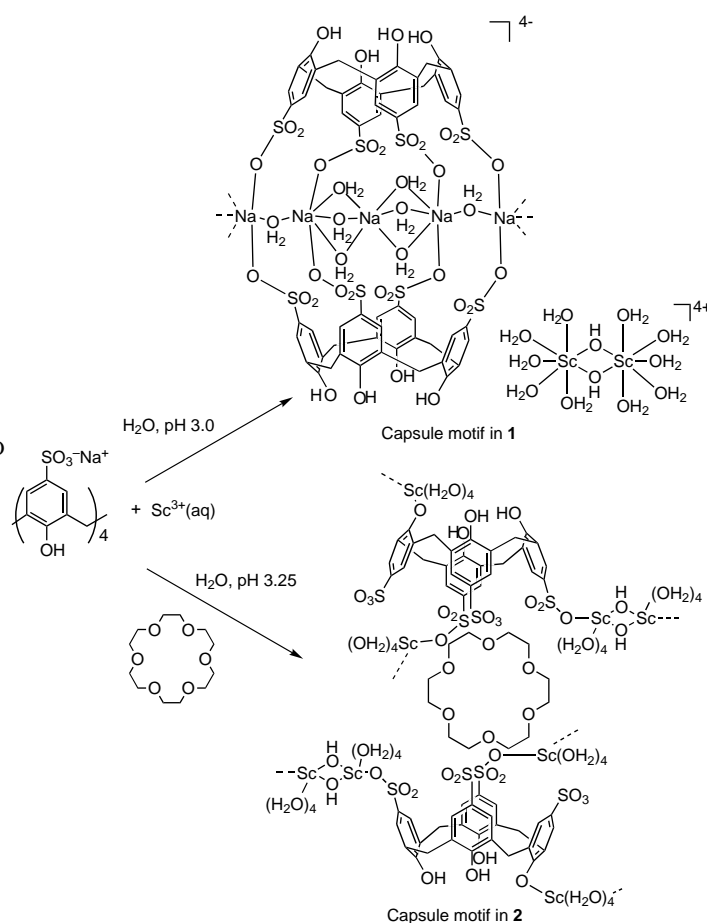
In **1**, seams of calixarenes are linked by an infinite chain of aquo-bridged sodium ions to create an array of capsules. A scandium dimer $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_{10}]^{4+}$ lies in water-laden channels between these arrays. In the structure acquired in the presence of [18]crown-6, scandium cations are bonded directly to the sulfonate and hydroxy groups of the calixarenes. The cations exist as both monomers and dimers, and link in two directions resulting in a two dimensional coordination polymer in the complex **2**. Unmetalated [18]crown-6 molecules are included in the cavities created by two calixarenes from different polymeric sheets. Thus host–guest interplay results in adding an extra dimension to the coordination framework as well as forming a capsule motif.



Results and Discussion

The complexes **1** and **2** crystallize from acidic aqueous solutions of sodium *p*-sulfonatocalix[4]arene, and scandium(III) tris-triflate (pH 3.0), or sodium *p*-sulfonatocalix[4]arene, scandium(III) tris-triflate and [18]crown-6 (pH 3.25), respectively, over several weeks (Scheme 1). More absorptions than are usually caused by equivalent sulfonate groups^[12] were observed in the 1400–1000 cm^{-1} range in the IR spectrum, which suggests that there are several different metal–sulfonate coordination environments in each structure. Whilst four absorptions are usually clearly visible in this region of the spectra (1193 vs, 1122 s, 1105 s, 1048 vs cm^{-1}), seven absorptions are apparent in the spectrum acquired from complex **1** (1306 w, 1267 m, 1244 m, 1211 s, 1168 vs, 1122 s, 1046 vs cm^{-1}) and five absorptions are present in the spectrum of complex **2** (1266 m, 1211 m, 1151 s, 1107 s, 1039 vs cm^{-1}). The presence of more absorptions in the spectrum of **1** with a one dimensional polymer indicates that it is of lower symmetry than the two-dimensional polymer of **2**. The structures were determined by single-crystal x-ray diffraction.

Details of the structure of **1** are shown in Figure 1 and Figure 2. There are three crystallographically distinct sodium ions present, all of which are octahedrally coordinated and bind to oxygen atoms at distances ranging from 2.337(2) to 2.587(4) Å (Figure 1). These distances are typical for Na–O coordination bonds.^[13] One type of sodium ion resides at the center of two calixarene molecules that form a capsule assembly and bridges to two crystallographically identical sodium ions on either side through bridging water molecules. These each bind another three bridging water molecules, and coordinate to one sulfonate group of an upper calixarene and one of a lower calixarene in a *trans* arrangement. The overall assembly is a calixarene capsule with a central aquo-bridged sodium trimer. The peripheral sodium atoms form a link to the third type of Na^+ ion through a water bridge, which hinges four different calixarenes belonging to two different capsules resulting in an infinite one-dimensional array of sodium ions and capsules (Figure 1). The molecular cavity of each calixarene on either side of the



Scheme 1. Synthesis of **1** and **2**.

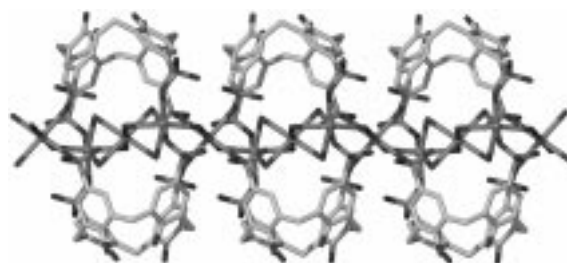


Figure 1. Crystal structure **1**. Section of the one-dimensional coordination polymer formed by calixarenes and aquo-bridged sodium cations. Three monomer units, consisting of a bis-calixarene capsule around a central aquo-bridged sodium trimer, are shown, linked by aquo and sulfonate coordination to a further sodium cation.

sodium array includes a single water molecule; the oxygen to arene centroid distances range from 3.46 to 3.72 Å, which is consistent with non-classical hydrogen bonding with the π electrons of the arene rings.^[14] Whilst structures involving sodium ions linked by oxygen-based bridges are not uncommon, these are usually in the form of oligomeric clusters^[15] or steplike polymeric arrays.^[16] The only structurally authenticated example of a sodium cluster interacting with a calixarene is within a biological pore mimic constructed from an oxacalix[3]arene.^[17] In the present structure there are two Na^+ ions per calixarene, which are in the 4– state. The charge on the capsules is balanced by a dimeric hydroxide-bridged

scandium counterion, $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_{10}]^{4+}$, in the crystal lattice. Each metal center in the scandium counterion is seven-coordinate with two μ -hydroxy bridges and five terminal water ligands. The bond lengths and angles are consistent with those previously reported for $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_{10}]^{4+}$ as its benzene sulfonate salt.^[18] The scandium dimers in the present structure are held in hydrophilic seams of alternating hydrophilic–hydrophobic bilayers, which are defined by protruding sulfonate and hydroxide groups from the calixarenes (Figure 2). Numerous water molecules of solvation also exist in this seam.

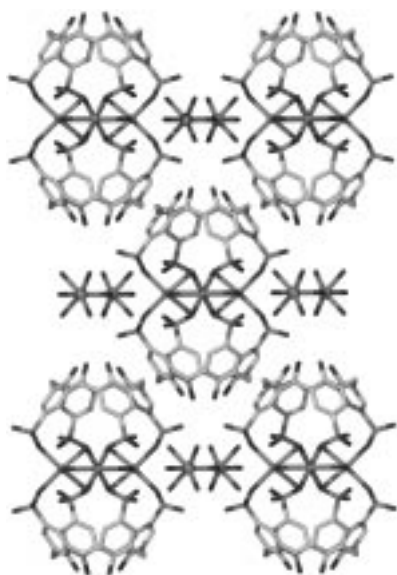


Figure 2. Packing diagram for **1**, illustrating π stacking between calixarenes of adjacent coordination polymers and the scandium dimers $[\text{Sc}(\text{OH})_2(\text{H}_2\text{O})_8]^{4+}$ occupying the hydrophilic seam between the calixarenes. Solvent water molecules are also present in this seam but have been omitted for clarity.

Details of the structure of **2** are shown in Figure 3 and Figure 4. Though the structure of **2** also contains the bis-calix[4]arene capsule motif and coordination polymers, they are constructed in a very different manner to those in the previously described linear array. The coordination polymer in **2** features calixarene ligands linked through scandium cations, and the structure is two-dimensional due to the presence of scandium cations in two distinct coordination environments (Figure 3). The first scandium cation is ligated in an octahedral manner; four terminal water ligands occur at $\text{Na}-\text{O}$ distances ranging from 2.110(7) to 2.162(7) Å, in addition, the metal ion binds a sulfonate group of one calixarene ($\text{Sc}-\text{OSO}_2$ 2.074(7) Å), as well as a phenolate group of an adjacent calixarene *cis* to the sulfonate group ($\text{Sc}-\text{OH}$ 1.995(7) Å). Each calixarene binds to a scandium ion through one phenolic oxygen, indicating a single phenolic deprotonation per calixarene, giving it a 5⁻ charge. This is consistent with other solid-state and solution studies which show that the first phenolic proton is removed at pH 3.2–3.5.^[19] The second type of scandium cation is a scandium dimer. As with the dimer seen in complex **1**, it consists of two seven-coordinate Sc^{3+} ions linked by two μ -hydroxy bridges

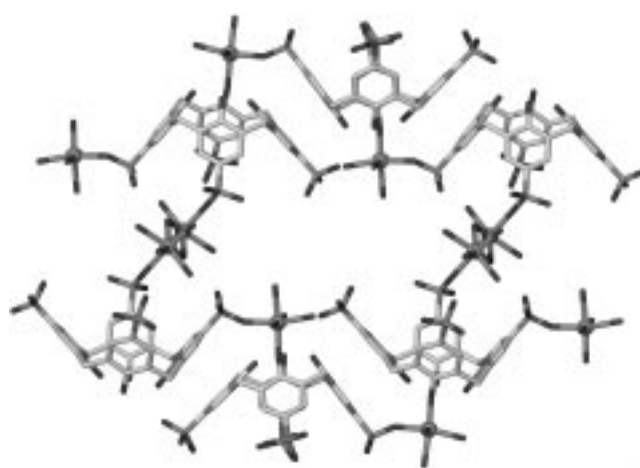


Figure 3. Section of the crystal structure of **2**, illustrating the coordination of scandium cations to calixarenes to create a two-dimensional coordination polymer. The monomeric scandium species coordinates to phenolic and sulfonate groups of adjacent calixarenes in a *cis* arrangement, while the scandium trimer bridges between two calixarenes in a *trans* fashion.

($\text{Sc}-\text{OH}$ 2.067(6) and 2.097(7) Å). However, in this case each metal ion is ligated by four terminal water molecules ($\text{Sc}-\text{OH}_2$ 2.142(7)–2.253(7) Å), and a sulfonate group of a calixarene through an oxygen atom ($\text{Sc}-\text{OSO}_2$ 2.154(7) Å). Hence the hydroxy-bridged scandium dimer acts as a bridge between two calixarenes.

Each calixarene is linked to three other crystallographically equivalent calixarenes to form a two-dimensional coordination polymer. The network can be described as chains of calixarenes in the familiar up/down bilayer arrangement, cross-linked by the scandium dimer to form a grid. Within the bilayer chains, the calixarenes are joined through the *cis* RO-Sc-O-S-O linkage, and also show π - π interactions, with arene-centroid separations of 3.76 Å. This parallels the combination of π -stacking and R-OH...O-S-O hydrogen bonding that is often observed within the *p*-sulfonatocalix[4]-arene bilayer packing.^[8] Collectively they form channels in which numerous water molecules of solvation are also present. Sheets of this two-dimensional coordination polymer pack together in a wavelike contour through hydrogen bonding and host–guest interactions (Figure 4a). The [18]crown-6 molecules lie between these undulous layers and effectively contribute a third dimension to the coordination polymer. Whilst host–guest chemistry has previously been used to construct one-dimensional molecular networks from calixarenes,^[4] this is the first time it has been exploited to append a third dimension to a two-dimensional coordination polymer. The crown ether is sandwiched by an ‘up’ and a ‘down’ calixarene from two neighboring sheets to create a capsule held together by a variety of supramolecular interactions (Figure 4b). In addition to favorable van der Waals forces associated with complementary curvature, there is hydrogen-bonding between aquo ligands of the Sc dimer and crown ether oxygen atoms at $\text{O}\cdots\text{O}$ distances ranging from 2.75 to 2.99 Å, as well as between hydroxy and aquo ligands of the scandium dimer and calixarene sulfonate groups on adjacent coordination polymers ($\text{O}\cdots\text{O}$ distances of 2.65 to 3.09 Å). Interestingly, the cavity of the crown ether remains

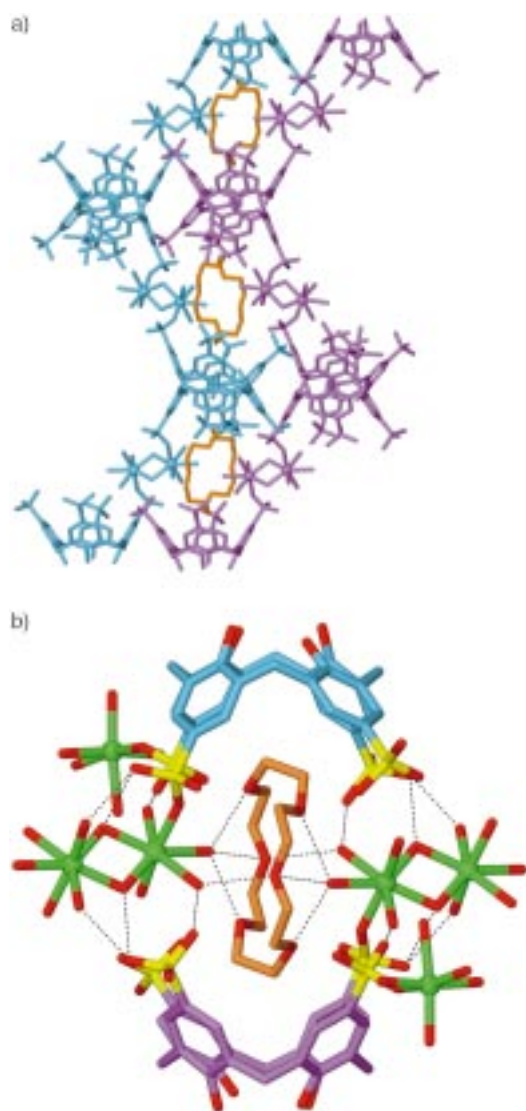


Figure 4. Crystal structure of **2**. a) Packing diagram showing two polymeric sheets packing in a wavelike contour around molecules of guest [18]crown-6. One coordination polymer is shown in blue, another in pink. Solvent waters are omitted for clarity. b) Detail of the capsule assembly around a crown ether molecule as shown in a; numerous intermolecular contacts consistent with hydrogen bond formation are shown as dotted lines.

void despite the presence of Na^+ ions in the reaction solution. Whilst Na^+ ions have proved to be of appropriate size for inclusion into the cavity of [18]crown-6,^[20] they have not played a role in any of the assemblies obtained by reaction of the rare-earth trications, [18]crown-6 and sodium *p*-sulfonatocalix[4]arene.^[7, 8] This may be because the excess of crown ether used in these reactions lowers the concentration of free sodium ions. Alternatively, the strength of the supramolecular forces holding the crown in the assembly may effectively compete against binding of sodium ions. Whatever the case, the result is a highly porous polymeric material studded with inclusion-ready cavities.

Conclusion

The coordination properties of the scandium trication and degree of acidity of the reaction solutions have provided

access to two unusual coordination polymers of different dimensionality. In each, two water-soluble *p*-sulfonatocalix[4]arenes come together to form a capsule motif, the claylike bilayer is maintained in the extended structure, and the resulting polymers are highly porous. This latter feature suggests possible functions for the coordination polymers, and future efforts will be directed at exploring their inclusion ability.

Experimental Section

Synthesis of $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_{10}][\text{Na}_4(\text{H}_2\text{O})_8[\text{calix}[4]\text{arene}(\text{SO}_3)_4]_2] \cdot 13\text{H}_2\text{O}$ (1**):** Scandium trifluoromethanesulfonate nonahydrate (10 mg, 15 μmol) and sodium *p*-sulfonatocalix[4]arene (8 mg, 9.6 μmol) were dissolved in water (250 μL ; pH 3). After several weeks, colorless crystals of **1** grew (3 mg, 25%). Electron microprobe analysis of **1** revealed the presence of scandium and sulfur in the ratio of 1:4. IR: sulfonate absorptions: $\tilde{\nu} = 1306\text{w}, 1267\text{m}, 1244\text{m}, 1211\text{s}, 1168\text{vs}, 1122\text{s}, 1046\text{vs cm}^{-1}$; elemental analysis (%) calcd for $\text{C}_{56}\text{H}_{104}\text{O}_{65}\text{Na}_4\text{S}_8\text{Sc}_2$: C 29.8, H 4.6, Na 4.1; found: C 30.2, H 3.4, Na 3.8.

Synthesis of $[\text{Sc}_2(\mu\text{-OH})_2(\text{H}_2\text{O})_8][\text{Sc}(\text{H}_2\text{O})_4]_2[\text{calix}[4]\text{arene}(\text{SO}_3)_4\text{H}^-]_2[\text{18}]\text{crown-6}] \cdot 16\text{H}_2\text{O}$ (2**):** [18]crown-6 (8 mg, 30 μmol) and sodium *p*-sulfonatocalix[4]arene (8 mg, 9.6 μmol) were dissolved in water (1 mL), then scandium trifluoromethanesulfonate nonahydrate (10 mg, 15 μmol) was added to the reaction solution (pH 3.25). After several weeks, colorless crystals of **2** grew (4.2 mg, 35%), which were highly sensitive to solvent loss. Electron microprobe analysis of **2** revealed the presence of sulfur and scandium in a ratio of 2:1. The IR spectrum indicates that structure **2** is of higher symmetry than structure **1**. IR: sulfonate absorptions: $\tilde{\nu} = 1266\text{m}, 1211\text{m}, 1151\text{s}, 1107\text{s}, 1039\text{vs cm}^{-1}$.

Crystal structure determinations: X-ray data for **1** and **2** were collected at 123(1) K on an Enraf-Nonius KappaCCD single-crystal diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on $|F^2|$ using SHELXL-97 by the X-Seed interface. The C–H hydrogen atoms were fixed at geometrically estimated positions. All non-hydrogen atoms were refined anisotropically with the exception of several oxygens belonging to disordered water molecules in structure **2**. Summaries of crystal data and refinements are given in Table 1. The x-ray powder

Table 1. Crystal structure data and details of structure refinements for **1** and **2**.

	1	2
formula	$\text{C}_{14}\text{H}_{26}\text{O}_{16.25}\text{Na}_1\text{S}_2\text{Sc}_{0.5}$	$\text{C}_{34}\text{H}_{64}\text{O}_{36}\text{S}_4\text{Sc}_2$
M_r [g mol^{-1}]	563.94	1267.01
crystal system	monoclinic	monoclinic
space group	$C2/m$	$P2_1/n$
a [\AA]	18.4317(4)	11.6002(2)
b [\AA]	26.0293(6)	29.7736(6)
c [\AA]	10.9047(2)	15.3681(3)
β	121.001(1)	95.165(1)
V [\AA^3], Z	4484.4(2), 8	5286.3(2), 4
ρ_{calcd} [g cm^{-3}]	1.671	1.592
crystal description	petal-shaped	rectangular
crystal size [mm]	$0.30 \times 0.25 \times 0.025$	$0.25 \times 0.125 \times 0.025$
μ [mm^{-1}]	0.48	0.518
$F(000)$	2348	2648
T [K]	123(1)	123(1)
2θ max [$^\circ$]	56.58	50.00
reflections collected	33811	64563
unique reflections	5679	9300
R_{int}	0.047	0.106
observed data $I > 2\sigma(I)$	4623	7028
parameters	322	692
R_1 (obs data)	0.0643	0.1201
wR_2 (all data)	0.1774	0.3440
S	1.037	1.120
max shift/error	0.00	0.00

patterns of the bulk material coincided with the Lazy-pulverix powder patterns generated from the crystal structures. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication nos. CCDC-151314 (1) and CCDC-151315 (2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

Acknowledgements

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